FUNDAMENTALS OF TRANSITION METAL OXIDE REDUCTION WITH HYDROGEN

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Abstract

The metal growth during hydrogen reduction of NiO, CoO, and Fe_3O_4 is characterised by some common features in respect of mechanism, kinetics and structure. The growth rate of the metal phase obeys a linear relationship in these systems. It is proportional to the square root of the hydrogen pressure and is distinctly reduced by water vapour in the gas phase. The metal/oxide interface seems to be the site of preferred oxygen removal. Radial fissures are formed in the growing metal particles when reduced at low temperatures; at elevated temperatures a micropore system is formed.

A peculiar structural effect was found in magnetite reduction above about 630 °C: The contact between oxide and iron is periodically broken producing a metal structure with concentric fissures. A tentative interpretation of the effect is given assuming vacancy accumulation at the metal/oxide interface.

The investigations performed are fundamental in character. They contribute to the understanding of some details experienced in industrial processes: the rate retarding effect of water vapour accumulated in the gas phase, the minimum phenomenon in the reduction of iron ores, and the sticking of grains by transferred iron nucleation in fluidized beds at elevated temperature.

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I Introduction

The reduction of metal oxides with H_2 or CO at high temperatures has been the subject of intensive research work [1,2] . Thermodynamic equilibria are well known today, the overall kinetics have been measured for various oxides and commercial ores. Curiously, very much less information has been achieved with respect to interface reaction mechanism, the appertaining micro-kinetics, and their relation to structural changes occurring in the metal phase during reduction.

Examining the various experimental techniques available to perform reduction studies, it turns out that optical microscopy as an "in situ" method could provide new and interesting information on the early stages of the reduction reactions. This method enables the direct and continuous observation of the metal growth in the oxide's surface and documents microstructural changes proceeding in the metal itself. A sketch of the experimental facility is given figure 1. The maximum magnification of the microscope was 180 times. The other features and objectives are self-evident from the figure.

The present author and his coworkers have performed detailed studies on the hydrogen reduction of transition metal oxides by hot stage microscopy [3-8]. The main results of these extended investigations are presented in this report.

II Results and Interpretation

The photo series of figure 2 documents the growth of iron on a wüstite single crystal (100) plane. The experimental conditions were 800 °C and 15 vol.-%H_2, balance N_2 . The time indicated below the individual photos is the time in seconds from the beginning of the experiment. From the photosequence some noteworthy facts become evident:

- The metal nucleation is inhomogeneous in nature with respect to location and time as well.
- The metal particles grow steadily; their shape is circular. In this case, the growth rate of the diameter is 750 µm min^{-1} .
- Oxide and metal are on the same level of focus. Therefore, it can be concluded that the difference in the molar volume of oxide and metal is stored in a micropore system inside the growing metal particles.

The H_2-reduction of CoO to Co, of NiO to Ni, of Cu_2O to Cu, or of Fe_3O_4 to Fe proceed in a very similar manner. When plotting the radius of the growing particle as function of time, a strictly linear relationship was found for all experimental runs. This statement is illustrated in figure 3 for Cu, Co, Ni, and Fe reduced under identical conditions (T=300 °C, 13 vol.-%H_2) . The linear growth law was found to be valid until complete covering of the oxide surface with a metal layer.

At this point, some ideas on the reaction mechanism can be checked by experimental evidence:

- As a first approach it might be considered that oxygen is removed by hydrogen from the free oxide surface, that metal ions and electrons diffuse through the oxide to the growing metal particles, and that these components are incorporated finally into the metal lattice. The metal particles should be hemispheres in shape growing on top of oxide surface; their growth rate should be inversely proportional to the particle radius [9,10]. None of these predictions are in accord with the experimental results. Furthermore, this model is unable to explain the well known fact that the oxygen removal rate is very much accelerated with the emergence of the metal phase (the so called autocatalytic effect).

- The experimental results make it necessary to locate the preferred oxygen removal site to the interface between the metal and oxide. This idea reconciles the contradictions stated above.

III Reaction Model Considerations

Based on the experimental findings, the following assumptions are used to develop a model with respect to reaction rate:

- Thermodynamic equilibrium is established between the reducing gas and the surface of the growing metal particle. Adsorbed species may be H_2, H_2O, OH, O, H.

- The oxygen activity in the metal oxide in direct contact with the metal corresponds to the equilibrium value between both phases.

- The rate of oxygen removal from the oxide surface is very much lower than the rate at the metal/oxide interface.

These conditions are sketched in figure 4: A steplike change in oxygen activity is established at the metal/oxide interface. Two different reaction modes are discussed:

- According to reaction mode I it is assumed that adsorbed hydrogen molecules are involved in the limiting reaction step. It follows that

$$v_I = k_1 \cdot p_{H_2} \cdot \left[1 - \left(\frac{p_{H_2}}{p_{H_2O}} \right)_{eq} \cdot \left(\frac{p_{H_2O}}{p_{H_2}} \right) \right] . \qquad (1)$$

  The growth rate of the metal phase is then anticipated to be proportional to the hydrogen pressure in the gas phase.

- In reaction mode II, hydrogen atoms, H_{ad}, are thought to be reacting species in the rate determining step, so that

$$v_{II} = k_2 \cdot p_{H_2}^{1/2} \cdot \left[1 - \left(\frac{p_{H_2}}{p_{H_2O}} \right)_{eq} \cdot \left(\frac{p_{H_2O}}{p_{H_2}} \right) \right] . \qquad (2)$$

The growth rate should be proportional to the square root of the hydrogen pressure. This last reaction mechanism could give a certain understanding of the autocatalytic effect often observed in reduction kinetics: H_{ad} species are possibly formed on certain metals, but not on the surface of the corresponding oxides.

To clarify the reaction mode, a great number of experiments were performed at varied hydrogen pressure and temperature. It is seen from figure 5 that the growth rate of Fe on Fe_3O_4 is proportional to the square root of the hydrogen pressure, so that reaction mode II is verified in this case. The $p_{H_2}^{1/2}$ - dependence was also found in the Co/CoO- and the Ni/-NiO- system [5]. But instead, Cu grows on Cu_2O according to a $p_{H_2}^{1}$ - relationship, i.e. reaction mode I is operating [7].

The modes I and II predict a linear decrease of the reaction rate with an increasing p_{H_2O}/p_{H_2} - ratio in the gas phase, but the experimental observation shows clearly a more distinct deceleration. Figure 6 gives results of the measurements; the effect is very pronounced in the magnetite to iron reaction. To explain this effect it is thought that water vapour molecules could block the metal lattice sites in the interface otherwise free for metal atom assimilation. Assuming absorption equilibrium between metal and gas phase, a factor

$$f = \left(\frac{1}{1 + K \cdot p_{H_2O}} \right) \tag{3}$$

can be formulated, which has to be added as an additional term to the rate equation. The complete rate equation for reaction mode II then reads

$$\frac{dr}{dt} = k_1 \cdot p_{H_2}^{1/2} \cdot \left(\frac{1}{1 + K \cdot p_{H_2O}} \right) \cdot \left[1 - \left(\frac{p_{H_2}}{p_{H_2O}} \right)_{eq} \cdot \left(\frac{p_{H_2O}}{p_{H_2}} \right) \right] . \tag{4}$$

In the case of iron growth on magnetite below 630 °C, the evaluation of the experimental results produced quantitatively

$$k_1 = 7{,}62 \cdot 10^3 \cdot \exp\left(-\frac{8\,488}{T} \right) \left[\mu m \cdot min^{-1} \cdot Pa^{-1/2} \right] \tag{5}$$

and

$$K = \exp\left(\frac{2\,385}{T} - 8{,}1 \right) . \tag{6}$$

The iron growth in depth of the oxide is the same as its lateral growth in the oxide's surface as long as diffusion of gaseous species through the pore system of the iron layer does not come into play. On this basis, a connection between these research results to those of gravimetric investigations can be established.

IV Microstructural Phenomena

The investigations of early stages of transition metal oxide reduction with hydrogen revealed some more features of the metal phase morphology. When decreasing the reaction temperature below a certain level, radial fissures form in the metal phase. As an example, two photo series related to the NiO reduction are shown in figure 7 . The circumference of the metal particle is firmly connected with the oxide, but during low temperature reduction broad fissures spread radially from the particle centre. The same effect was also found in the Fe/ Fe_3O_4- and the Co/CoO- system. The said temperature limit is identical to the strain recovery temperature of the metal in question. The linear growth law was also found to be valid in the low temperature reaction range.

In the reduction of magnetite at rather high temperatures, a third entirely unexpected effect was found. According to the comparative SEM-images of figure 8 concentric fissures now appear in the metal phase. The growth is no longer continuous but is interrupted instead by periodic halts, which can take several minutes until a new growth push takes place. In the SEM image it is seen that the contact between the metal and the oxide is lost. At such sites the autocatalytic reaction effect cannot work, so the metal growth stops. The interpretation of this peculiar growth mechanism is still tentative: possibly it is bound to the existence of a thin, intermediate wüstite layer, thermodynamically stable above 570 °C. During the growth pulse of the metal phase a high flow of iron ion vacancies (and electrons) is established across the wüstite layer. Possibly the void accommodation into the pore system of the metal is deranged under these extreme conditions so that the contact between metal and oxide breaks down.

Figure 9 is an Arrhenius plot of the experimental results on magnetite reduction. At low temperatures radial fissures develop in the metal phase, at intermediate temperatures only micropores exsist. At temperatures above the limit of about 630 °C the discontinuous stop and go-mechanism starts, producing a minimum of the growth rate at about 750 °C. This minimum phenomenon in magnetite reduction is well known and has hitherto been the subject of many speculations.

V Conclusions

The research results discussed are fundamental in character. Nevertheless they contribute to the understanding of industrial experience: the reduction rate produced by hydrogen is decreased distinctly by merely a small accumulation of water vapour in the gas phase; metal nucleation can be transferred from oxide grain to oxide grain during contact in fluidized beds, metal bridging may then give rise to the sticking effect; on the other hand, fissures between oxide and metal abrogate the catalytic effect, producing low reduction rate in a wide range of temperature.

References

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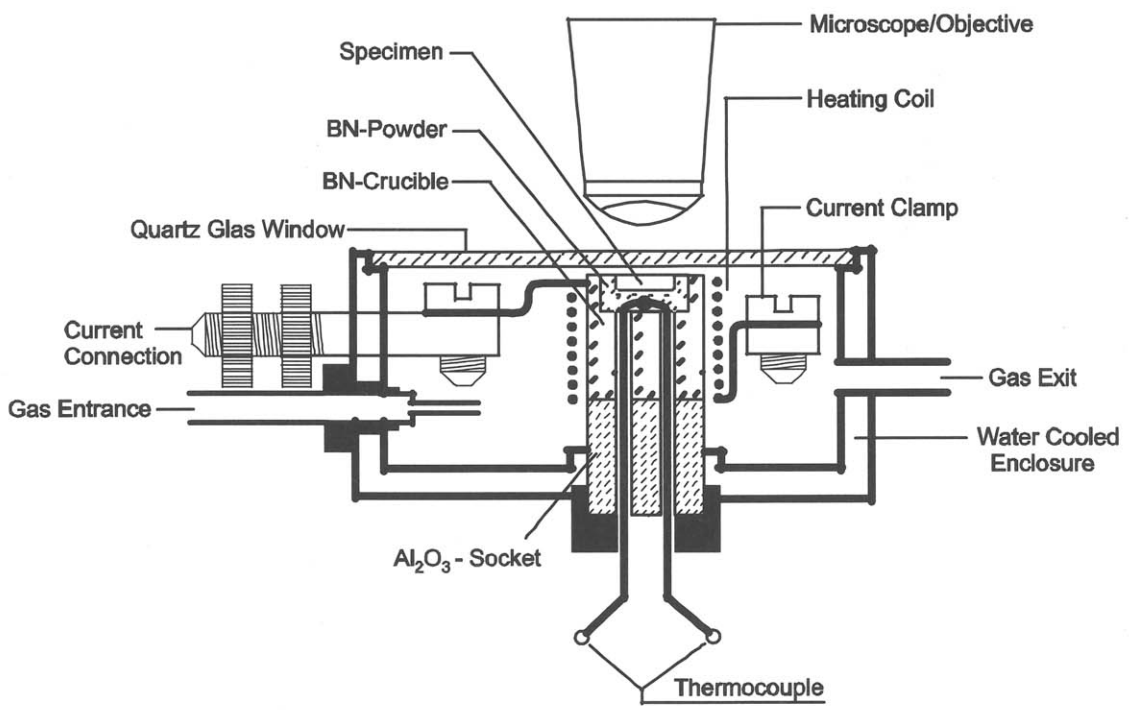


Figure 1. Hot Stage Microscopy, Set-Up of the Reaction Chamber

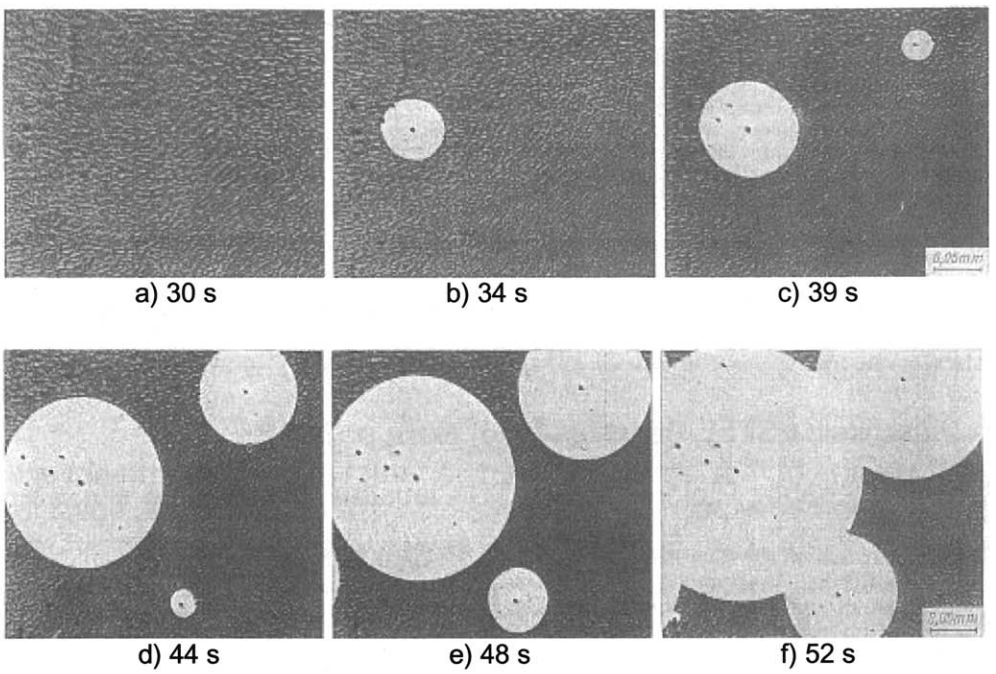


Figure 2. Iron Particles Growing on Wüstite (100)-Plane

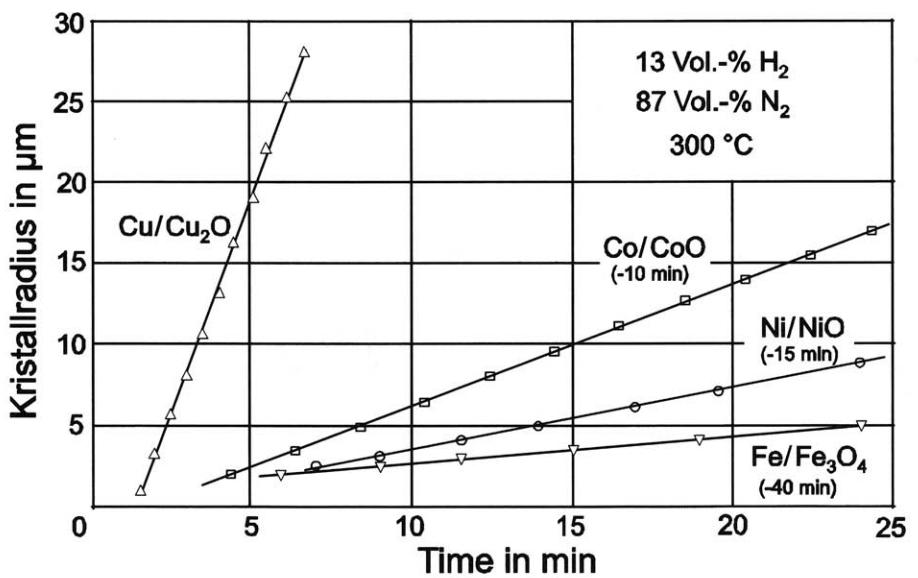
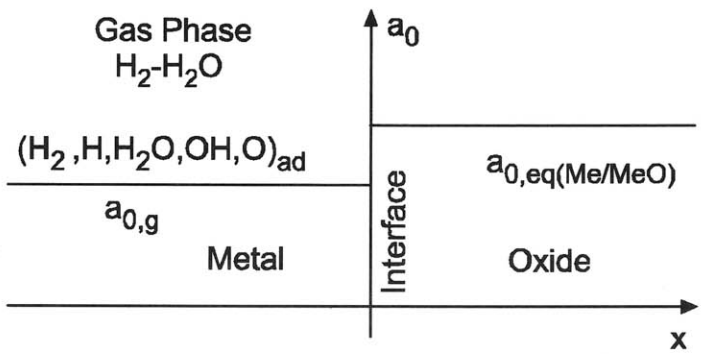


Figure 3. Linear Growth of the Metal Phase during Reduction with Hydrogen



I $$H_{2,ad} + MeO \longrightarrow H_2O_{ad} + Me$$

$$v_I = \vec{k}_I \cdot p_{H_2} - \overleftarrow{k}_I \cdot p_{H_2O}$$

$$\boxed{v_I = k_I \cdot p_{H_2} \left[1 - \left(\frac{p_{H_2}}{p_{H_2O}}\right)_{eq} \cdot \left(\frac{p_{H_2O}}{p_{H_2}}\right)\right]}$$

II $$H_{ad} + MeO \rightarrow OH_{ad} + Me$$

$$v_{II} = \vec{k}_{II}\, \Gamma_H - \overleftarrow{k}_{II}\, \Gamma_{OH} = \vec{k}'_{II} \cdot p_{H_2}^{1/2} - \overleftarrow{k}'_{II}\, \frac{p_{H_2O}}{p_{H_2}^{1/2}}$$

$$\boxed{v_{II} = k_{II} \cdot p_{H_2}^{1/2} \left[1 - \left(\frac{p_{H_2}}{p_{H_2O}}\right)_{eq} \cdot \left(\frac{p_{H_2O}}{p_{H_2}}\right)\right]}$$

Blocking of metal growth sites by water vapour absorption

$$v = f \cdot v_{I,II} \qquad f = \frac{S_f}{S_f + S_b} = \frac{1}{1 + \frac{S_b}{S_f}}$$

$$H_2O + S_f \rightleftharpoons S_b \;; \qquad K = \frac{S_b}{S_f \cdot p_{H_2O}} \;; \qquad \boxed{f = \frac{1}{1 + K \cdot p_{H_2O}}}$$

Figure 4. Interface Reaction Mechanism and Particle Growth Rate

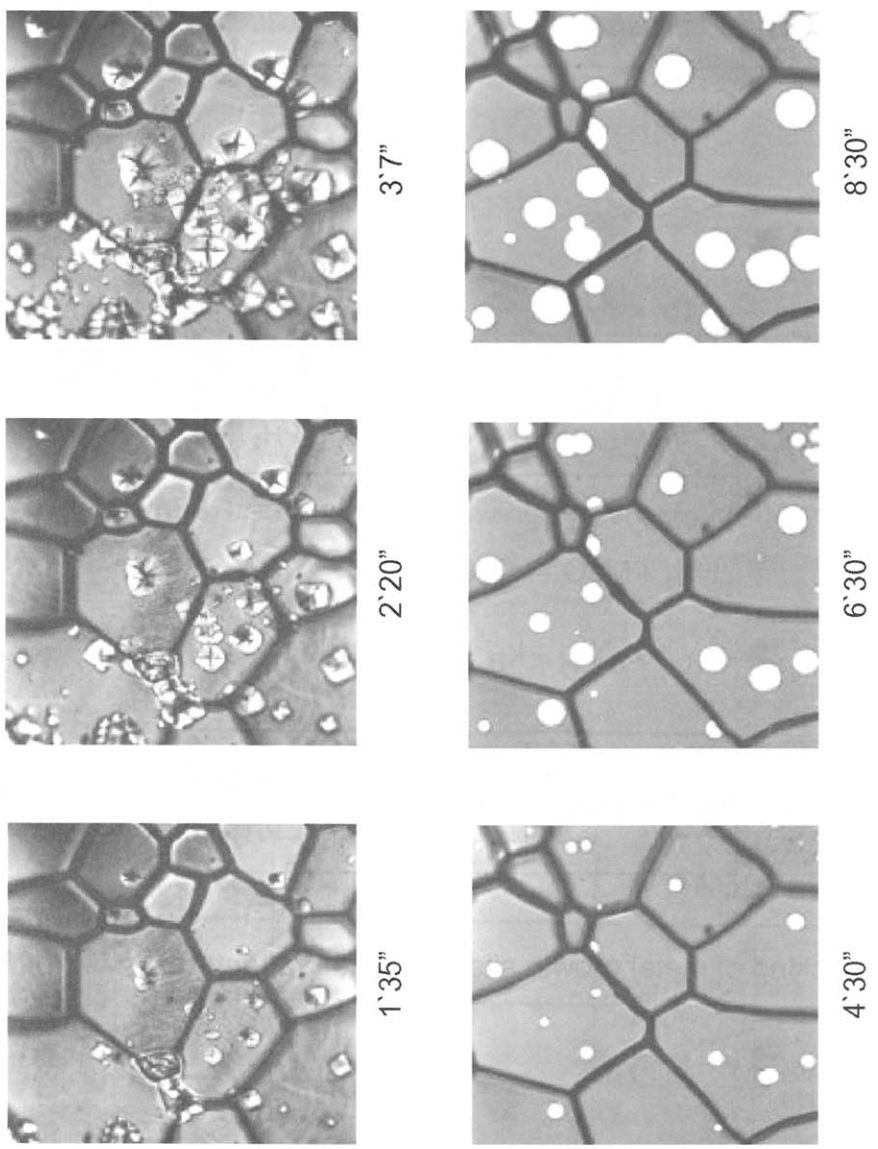


Figure 5. Growth of Nickel on Nickeloxide

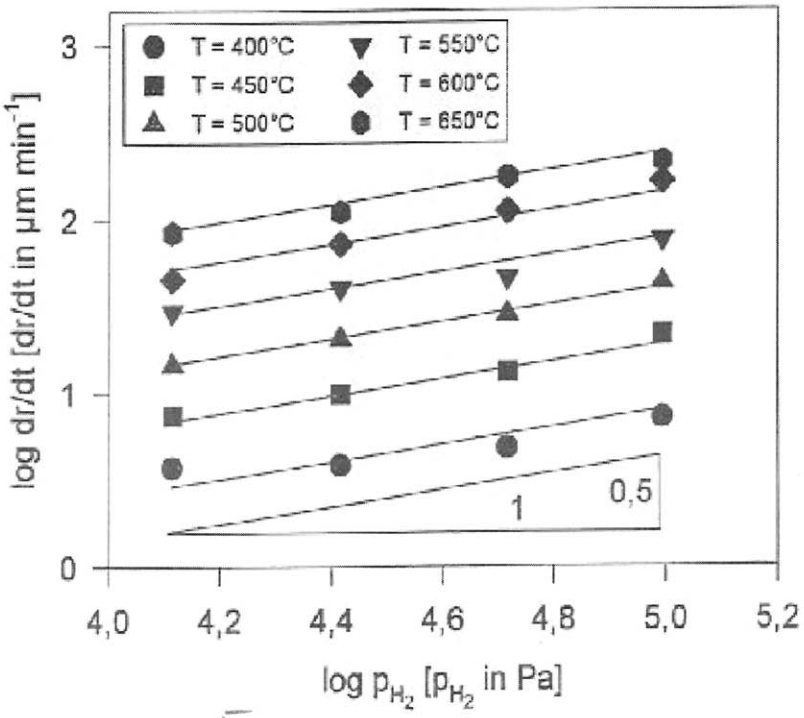


Figure 6. Growth Rate of Iron on Magnetite

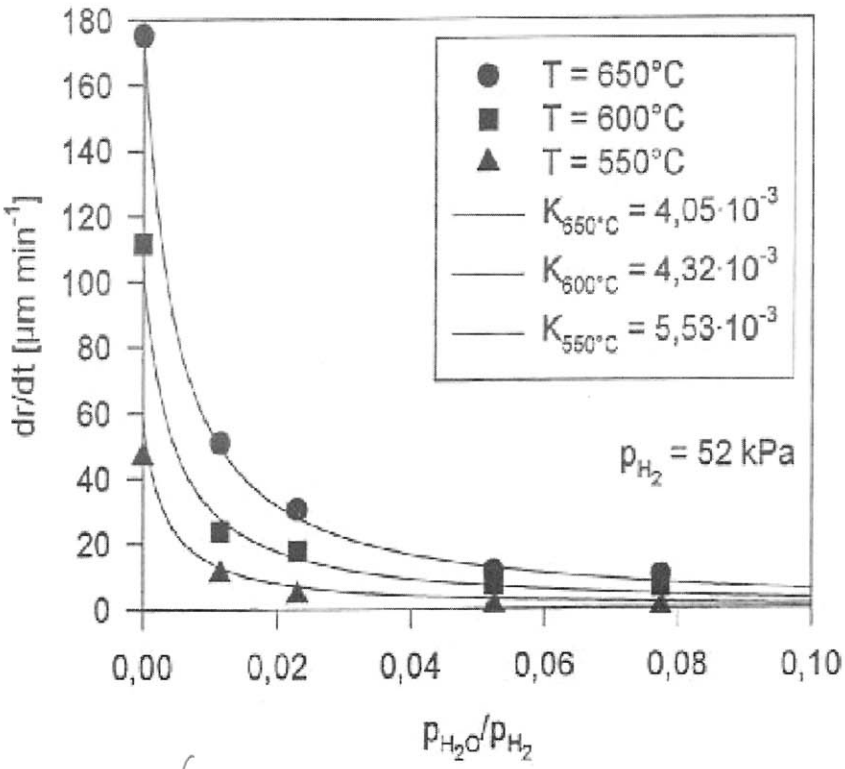


Figure 7. Reduction of Magnetite, Influence of Water Vapour on the Growth Rate of Iron

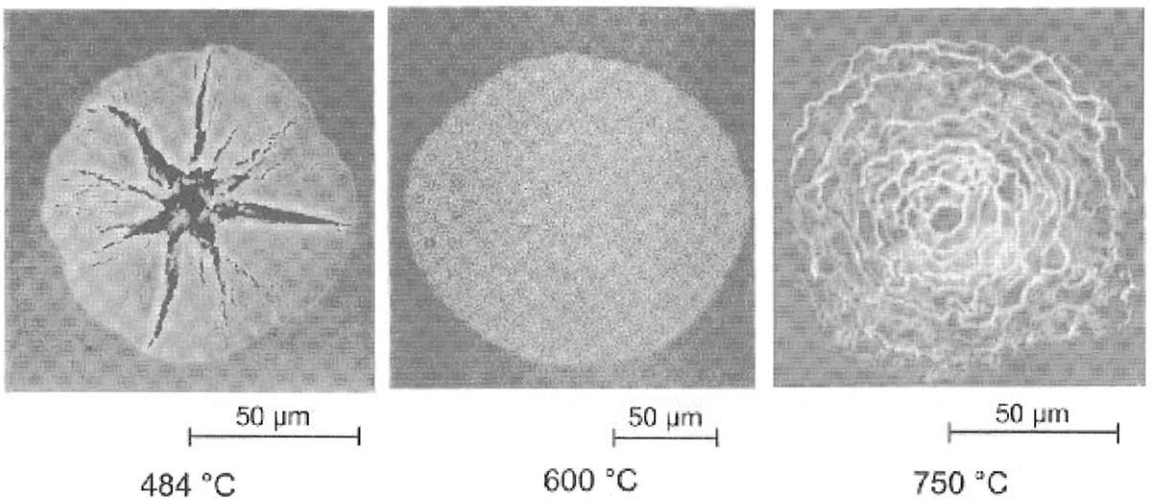


Figure 8. Growing Iron Particles on Magnetite

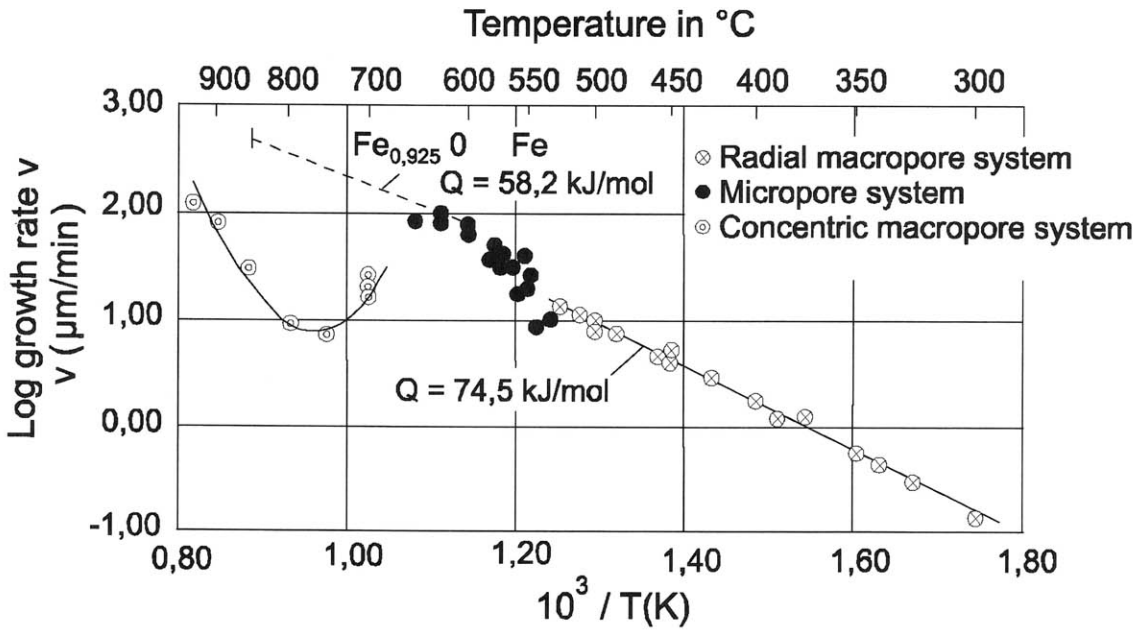


Figure 9. Growth Rate of Iron on Magnetite